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# Carbon: The 129-Year Controversy Over the Solid Liquid-Vapor Triple Point

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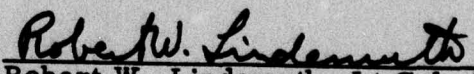
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## CARBON: THE 129-YEAR CONTROVERSY OVER THE SOLID-LIQUID-VAPOR TRIPLE POINT

The controversy over the solid-liquid-vapor (S-L-V) triple point of carbon started in 1849<sup>1</sup>. Since that time, investigators in this field have developed widely differing points of view. Some believe the triple-point pressure is  $\sim 10^5$  Pa ( $\sim 1$  atm), whereas others believe it is  $\sim 10^7$  Pa ( $\sim 100$  atm). Over the past approximately 40 years, the  $10^7$  Pa view has been dominant, but the evidence is not entirely convincing. In the past few years, new evidence has been obtained that appears to end the controversy at least from the standpoint of the proper order of magnitude of the pressure.

In any single-component phase diagram, the S-L-V triple point is located at the intersection of the solid-liquid (S-L) and solid-vapor (S-V) boundaries. These boundaries for carbon are shown in Fig. 1. The S-L boundary was obtained by an extrapolation of Bundy's high-pressure data, and the JANAF data gives the S-V boundary<sup>2,3</sup>. Even though Bundy's extrapolated data could be in error by one or two hundred degrees, these boundaries (Fig. 1) clearly indicate that the S-L-V triple-point pressure must be on the order of  $10^5$  Pa. However, the S-L-V triple point was believed to occur at  $\sim 10^7$  Pa and 4200 K, and it was considered possible that the JANAF calculations above  $\sim 3000$  K were in error. Thus, S-V boundaries, e.g., A in Fig. 1, were proposed, even though there was little experimental basis for doing so<sup>4</sup>. The question of whether or not the S-V boundary is correct can be answered by considering the results of several studies on the vapor pressure of carbon in the region of 4000 K.

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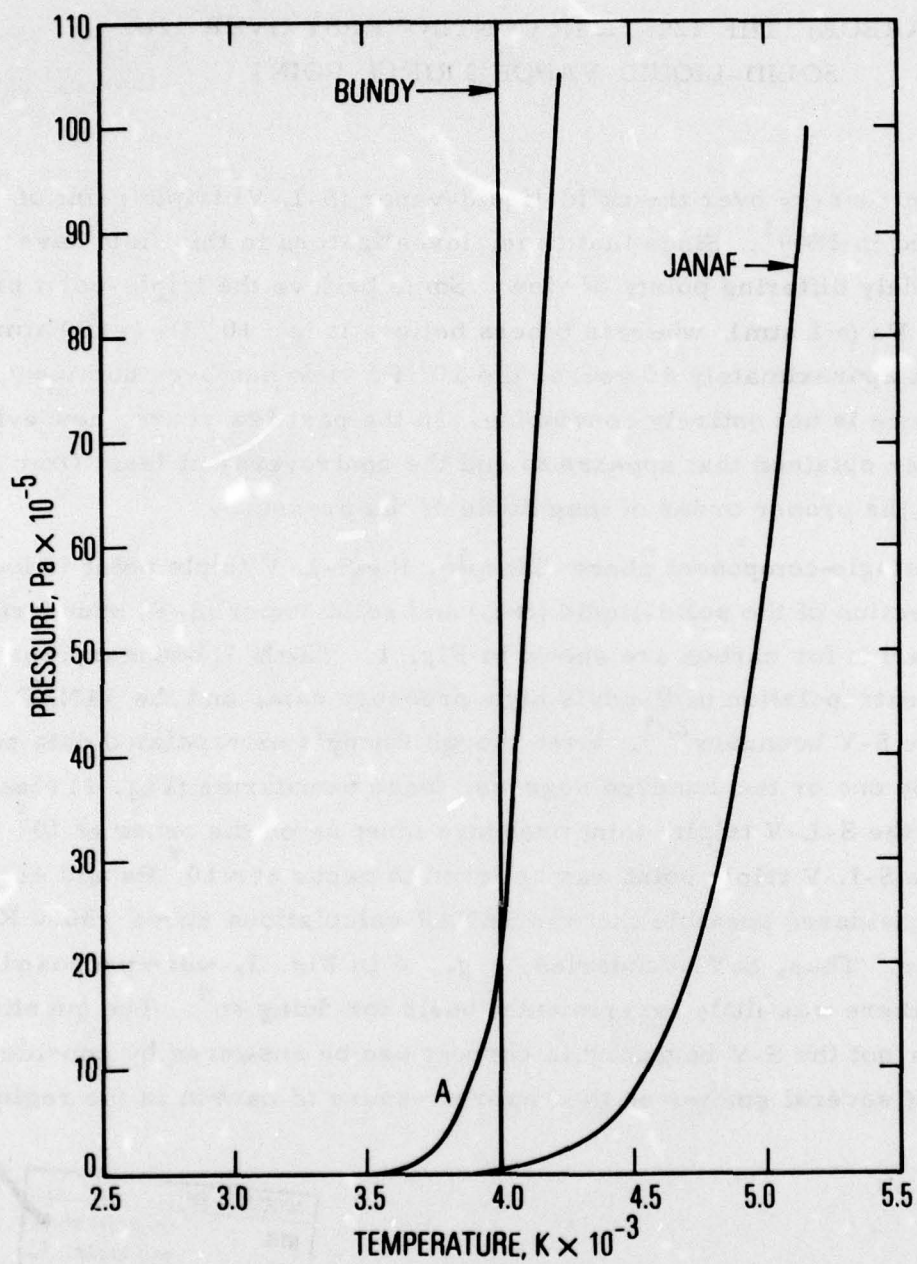


Figure 1. Solid-Liquid and Solid-Vapor Boundaries for the Low-Pressure Region of the Carbon Phase Diagram

A short time ago, Covington, Liu, and Lincoln<sup>5</sup> and Lundell and Dickey<sup>6</sup> obtained vapor pressure data that confirmed the JANAF data in the region of  $10^5$  to  $10^7$  Pa. Also, Maurer and co-workers<sup>7</sup> obtained data at  $\sim 10^4$  Pa that were in agreement with the JANAF curve. Data obtained several years ago by Whittaker and co-workers<sup>8-10</sup> indicated that graphite transforms to the more stable carbyne forms of carbon above  $\sim 2600$  K. Hence, the equilibrium S-V boundary must lie below the JANAF curve. All of these data are shown in Fig. 2 in the region of the S-L-V triple point. Recently, Whittaker<sup>11</sup> reported preliminary data on the rate of transformation of graphite into each of two of the carbyne forms<sup>11</sup>. These data also show that the lowest transformation temperature is  $\sim 2600$  K and further supports the conclusion that the equilibrium vapor pressure of carbon must be less than the JANAF values above this temperature. These rate data show that the transformation graphite  $\rightarrow$  carbyne is relatively slow up to 2800 K (first-order rate constant of  $\sim 10^{-5}$  / sec at 2800 K). There is some evidence that the transformation rates increase with temperature as expected, but 2 or 3 sec are required for 80 to 90% conversion in the region of 3800 K. Therefore, the transformation did not have time to take place in the experiments of Covington, Liu, and Lincoln because their measurement time was on the order of 1 msec or less. Hence, it would be expected that their data would fall on the JANAF curve because it represents the vapor pressure that graphite would have if it were the stable form above  $\sim 2600$  K. In the experiments of Lundell and Dickey, it is difficult to estimate the time required to heat and vaporize the carbon because the beam traversed through the sample at an appreciable rate. However, it appears that the time available for transformation of the carbon was well below 1 sec, especially at the higher power densities. Therefore, their data would be expected to fall on the JANAF curve. These five groups of data constitute a mutually consistent set that experimentally establishes the S-V curve in the region of 4000 K and rules out the possibility of an S-V curve as A in Fig. 1. With the S-V curve thus established, the only other way to get an S-L-V triple point at  $\sim 10^7$  Pa would be for Bundy's data to be in error by  $> 1000$  K, which is highly unlikely.



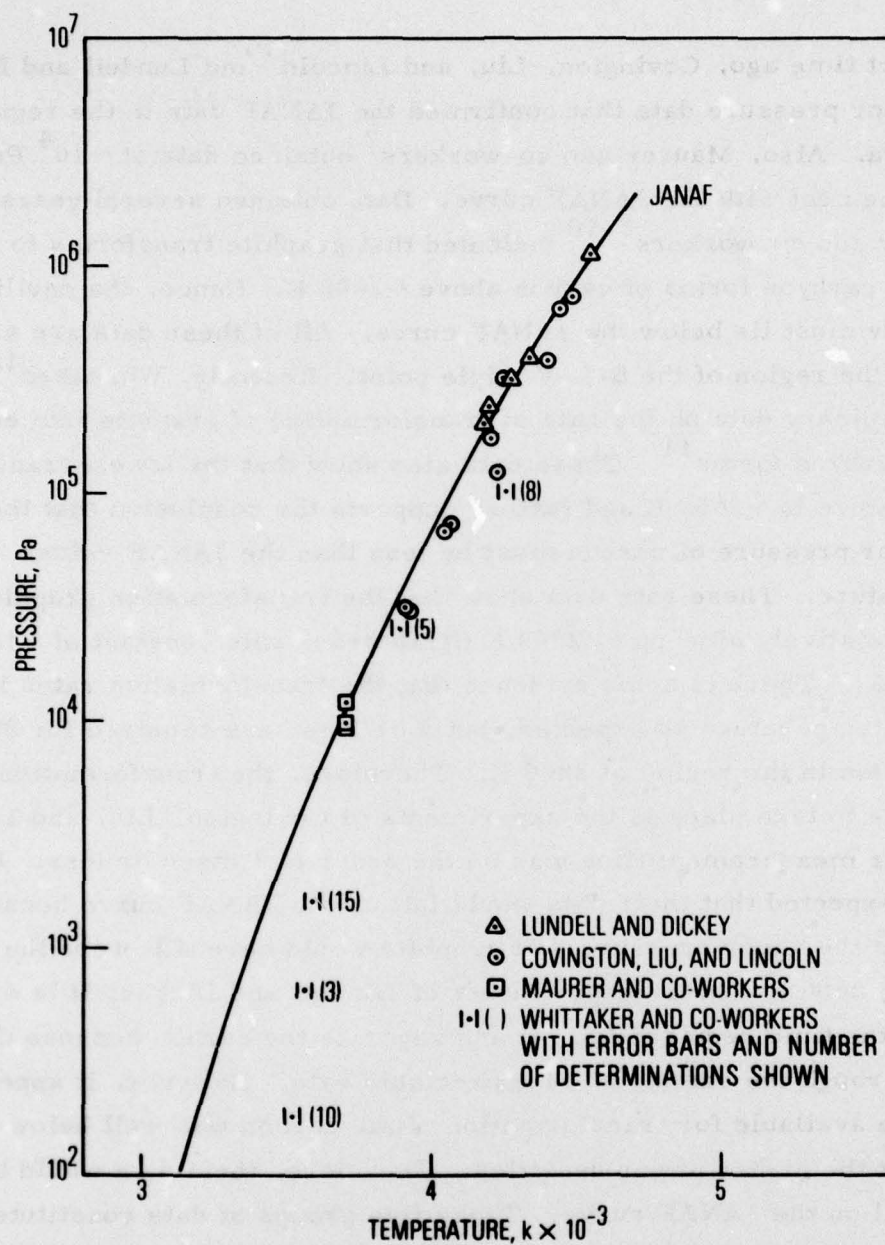


Figure 2. Vapor-Pressure Data for Carbon in the Region of the Solid-Liquid-Vapor Triple Point

If the S-L-V triple-point pressure of carbon occurs at  $\sim 10^5$  Pa, then it is reasonable to question the significance of the results obtained at  $\sim 10^7$  Pa. The pressures reported range from  $1.01 \times 10^7$  to  $1.22 \times 10^7$  Pa, but most values approximate  $1.01$  to  $1.03 \times 10^7$  Pa. Temperatures range from  $\sim 3970$  to  $4390$  K with no tendency to cluster about a particular value. All of these high-pressure results suffer from at least two major shortcomings: (1) In all cases, it was assumed that the carbon vapor pressure equilibrated with the pressurizing gas. This condition is not necessarily achieved, and some means must be provided to show that this equilibration has been achieved. Therefore, the pressures are suspect inasmuch as they are not really experimentally determined values but essentially assumed values. (2) No spectroscopy was carried out on the radiation that arrived at the pyrometer. It is necessary to assure that line or band emission is not causing spurious pyrometer readings and to show that the radiating gas surrounding the specimen is not optically dense. In the laser heating experiments of Whittaker and co-workers, much spectroscopy was carried out on the solid and gas phases. It was found that the carbon gas emits only Swan radiation. If impurities are present, additional lines or bands appear in the spectrum; hence, it is important to assure that the pyrometer uses a wave length range that is free of this radiation. Also, it was found that the optical density of the gas increases with pressure, and, at  $\sim 10^6$  Pa, the effect of the optical density is no longer negligible. At  $10^7$  Pa, the optical density would be quite high. Hence, it is possible that a pyrometer may not be able to "see" the surface of the condensed phase at this pressure. In this case, the reported temperatures would have little meaning. Indeed, the effect of high optical density could account for the wide range of reported temperatures.

One possible reason why the high-pressure data clusters in a general region is that a solid-solid-liquid triple point could exist near  $10^7$  Pa at point P in the proposed phase diagram (Fig. 3)<sup>10</sup>. In this case, the solid phases would have to be carbyne forms of carbon. Since the equipment used in the high-pressure work was not designed to study condensed phase equilibria, the



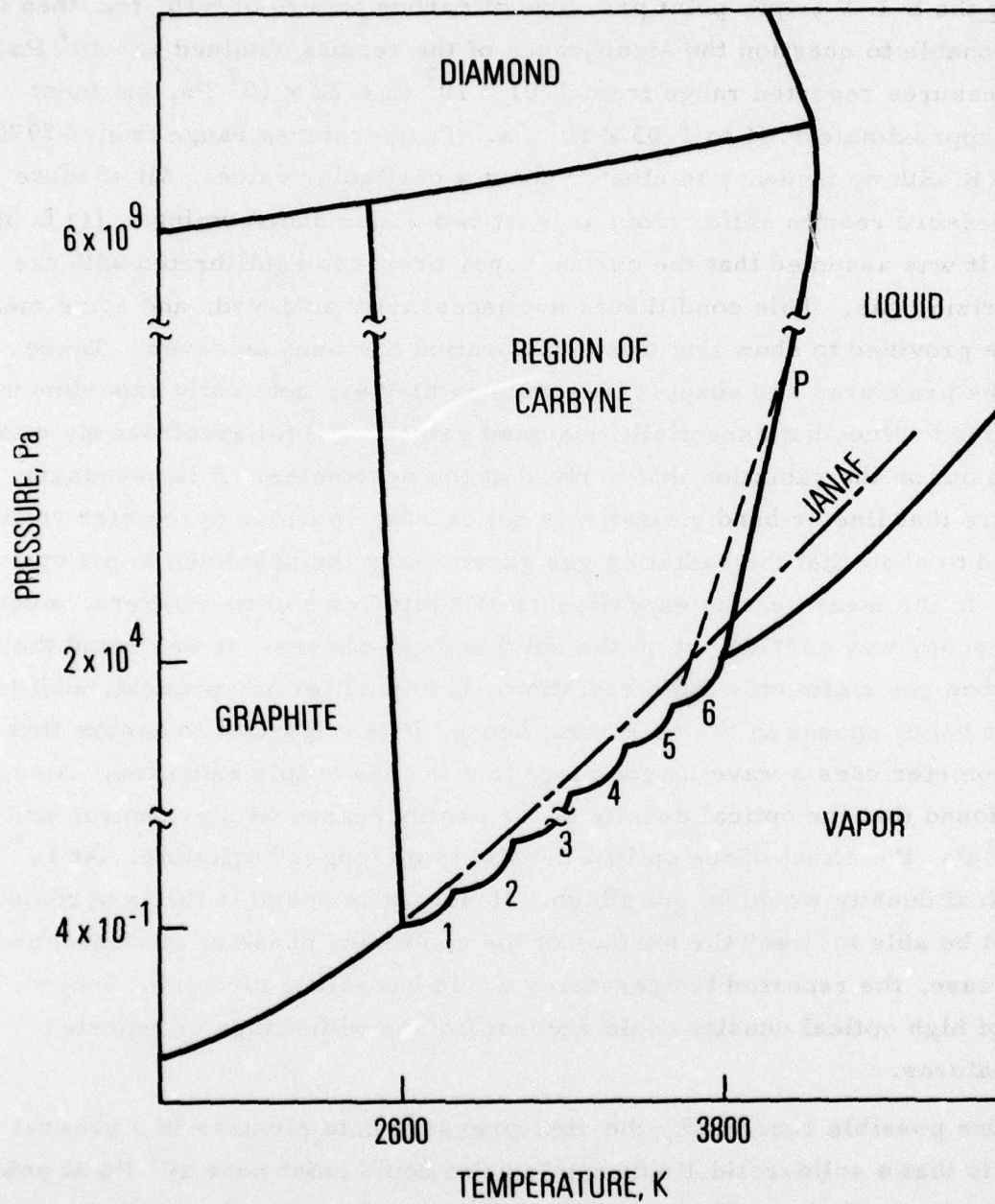


Figure 3. Proposed Carbon-Phase Diagram. From Ref. 10.

observed pressure and temperature would be some kind of average determined by the competition between the condensed-phase equilibrium and the liquid-vapor equilibrium attempting to coexist. This situation would result in a large scatter in reported temperatures and pressures because this competition would depend on the idiosyncrasies of each particular apparatus.

In view of the uncertainties discussed here, it is difficult to interpret the high-pressure results. However, the recent vapor-pressure data cited here, together with Bundy's high-pressure results, contribute to the inescapable conclusion that the S-L-V triple point of carbon occurs at a pressure on the order of  $10^5$  Pa, and that the reported results in the region of  $10^7$  Pa must refer to some other phenomenon.



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